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**IGNITION OF SOLID PROPELLANT  
CONTAINING AMMONIA AND OTHER  
FUELS BY PERCHLORIC  
ACID VAPOUR**

by

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WESTCOTT

Technical Report No. 66/8

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COMPOSITE SOLID PROPELLANT IGNITION: IGNITION OF AMMONIA AND  
OTHER FUELS BY PERCHLORIC ACID VAPOUR\*

by

G. S. Pearson

D. Sutton

SUMMARY

The ignition of polyisobutene, polyurethane, polystyrene and polymethylmethacrylate has been studied with oxygen gas and with perchloric acid vapour under the same experimental conditions. All these fuels ignited with perchloric acid vapour at 200-250°C whereas ignitions with oxygen were only achieved at temperatures above 350°C. Less volatile fuels such as carbon black, nylon and terylene also ignited with perchloric acid vapour at 200-250°C. Ignition of ammonia, methane, ethylene and isobutene was not achieved by perchloric acid vapour in the absence of a surface at 200-250°C. In the presence of a surface the order of decreasing ignitability was ammonia, isobutene, ethylene, methane. Cupric chromate and ferric oxide were effective catalysts in the ignition of gaseous fuels with perchloric acid vapour. Titanium dioxide, silica and alumina had no detectable effect. It is concluded that in ammonium perchlorate propellents the important reactions leading to ignition are heterogeneous rather than homogeneous, and that in a catalysed propellant the reaction of ammonia and perchloric acid on the surface of the catalyst is the significant reaction. The results are discussed in relation to current theories of the mechanism of the ignition of composite solid propellents containing ammonium perchlorate.

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\*Part of the work presented in this report was contained in R.P.E. Technical Memorandum No.377, November 1965.

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## 1 INTRODUCTION

During recent years there has been much interest in the mechanism of ignition of solid propellents, particularly in the ignition of composite propellents containing ammonium perchlorate as oxidizer. Two different mechanisms have been suggested on the basis of the experimental data obtained, one proposing that the important exothermic reactions which lead to ignition occur between fuel and oxidizer gases in the vapour close to the propellant surface, and the other proposing that the exothermic reactions occur between gaseous oxidizer and fuel at the propellant surface.

The first mechanism was proposed by McAlevy et al<sup>1</sup> following ignition experiments in a shock tube in which samples of polystyrene, and samples of composite propellant containing polystyrene as fuel and ammonium perchlorate as oxidizer, were ignited with hot oxygen gas under pressure. The surface temperatures of the polystyrene and propellant samples in these experiments were only about 160°C, which is much below the temperature at which ammonium perchlorate decomposes rapidly, and yet ignitions were achieved in only a few milliseconds. McAlevy believed that ignition occurred when vaporized fuel diffused from the surface and reacted with the oxygen which was at a temperature of about 1000°C.

Anderson et al<sup>2</sup>, following experiments on the hypergolic ignition of propellents with such oxidizers as fluorine and chlorine trifluoride, proposed the alternative mechanism that the essential "run-away" condition resulted from a heterogeneous reaction between oxidizer gases and the solid fuel. Furthermore, Anderson suggested that the dependence of ignition delay time on oxygen concentration, experimentally determined by McAlevy<sup>1</sup>, fitted the heterogeneous mechanism better than the homogeneous mechanism.

Recently, however, McAlevy<sup>3</sup> has produced experimental evidence to show that there is no reaction at a pressure of 200 lb/in<sup>2</sup> and a temperature of 200°C between oxygen gas and polystyrene. This supports his proposed mechanism, deduced from his shock tube experiments. McAlevy concluded that, whereas it is probable that thermo-chemical attack on a propellant surface by certain extremely powerful oxidizing agents, such as fluorine and chlorine trifluoride, could lead to ignition via a heterogeneous mechanism, it is highly unlikely that this mechanism is generally valid when less powerful agents, such as oxygen and perchloryl fluoride, are present.

It must now be pointed out that the gases produced by conventional solid propellant ignition systems are not oxidizer rich and therefore the oxidizing

species in the ignition reactions must be derived from the oxidizer in the propellant. In the case of ammonium perchlorate composite propellents it is well established<sup>4,5</sup> that the initial products of the decomposition of ammonium perchlorate are ammonia and perchloric acid and that this decomposition occurs at an appreciable rate at a temperature of about  $300^{\circ}\text{C}$ <sup>6</sup> with the commercial grade ammonium perchlorate used in propellents. Furthermore, Powling has recently affirmed<sup>7</sup> that at low pressure the flame above such a propellant is a premixed flame of perchloric acid, ammonia and the pyrolyzed fuel. In all therefore, the reactions to be considered in ignition are those between perchloric acid and ammonia, gaseous fuel or solid fuel.

Perchloric acid vapour, although not as powerful an oxidizer as fluorine and chlorine trifluoride, is much more reactive than oxygen<sup>8</sup>. It was therefore considered pertinent to determine whether it could produce ignitions with fuels over a range of temperatures extending below  $300^{\circ}\text{C}$ , or if ignition could occur only when the perchloric acid and vaporized fuel had diffused from the propellant surface into the higher temperature region of the igniter gases. The ignition of fuel by perchloric acid vapour has hitherto only been studied for simple gaseous fuels (hydrogen<sup>9</sup> and methane<sup>10</sup>).

In the present work, ignition studies have been made using both oxygen and perchloric acid vapour with solid fuels typical of those used in composite solid propellents. These have been extended to include gaseous fuels which may be expected to be present over the surface of such a propellant.

## 2 EXPERIMENTAL

### 2.1 Apparatus and techniques

#### 2.1.1 Solid fuels

The apparatus used for solid fuels was a modified version of that previously described<sup>11</sup> for the study of premixed flames of perchloric acid vapour at atmospheric pressure. The jacket tube was removed and the burner was bent so that the acid vapour emerged downwards from the end of a pyrex tube, 4 mm internal diameter.

The acid vapour was directed either into a  $2\frac{1}{4}$  inch long  $\frac{1}{2}$  inch diameter pyrex tube containing a sample of the fuel and heated by nichrome wire, or onto an unheated sample of fuel placed on a small watchglass at a distance of 1 inch from the acid vapour tube. Temperatures in the oxidizer flow and in the heated fuel tube were measured immediately before each experiment by chromel-alumel thermocouples, using a cold junction in ice.

The amount of fuel in each experiment was approximately a  $\frac{1}{4}$  inch cube. In the heated fuel experiments the sample was allowed to warm up for 30 seconds in the heated tube before introduction of the oxidizer. Once ignition was achieved, combustion was always sustained.

Oxygen was also passed through the same apparatus so that a comparison could be made. In each case the total flow rate was about  $25 \text{ cc sec}^{-1}$  at NTP. The oxidizer mixtures used were (i) 100% oxygen, (ii) 60% oxygen 40% argon and (iii) 22% perchloric acid, 48% water and 30% argon (per cent by volume). All experiments were carried out at atmospheric pressure.

### 2.1.2 Gaseous fuels

The apparatus used was a modified version of that for solid fuels and is shown in Fig.1. Perchloric acid vapour, diluted with about an equal volume of argon, and fuel streams were directed into a shallow depression in a ceramic plate. The glass tubes (i.d. 4 mm) supplying the gaseous reactants had flared ends so that the asbestos covered heating wires were shielded from the igniting gases. The tubes could be swung into position by rotation at ground glass joints. Temperatures were measured by chromel-alumel thermocouples, using a cold junction in ice. In experiments using the ceramic tile with the embedded thermocouples a continuous temperature record was obtained.

Ignitions with gaseous fuels were also studied in the absence of a surface by removing the ceramic tile and hot plate and allowing the reactant jets to impinge in the atmosphere. In some of the gaseous fuel experiments a clean glass rod (7 mm dia.) was introduced about 5-10 mm below the tubes to provide a surface. In the experiments with solid fuels and with catalysts, 30 seconds were allowed for the samples to warm up before the ignition tests were made.

It is convenient to designate the basic experimental arrangements as A, B, C and D in the following way:

- A: Solid fuel apparatus (acid vapour directed into a closed tube).
- B: Apparatus in Fig.1. Ceramic tile and hot plate present.
- C: As B, but ceramic tile and hot plate removed.
- D: As C, but with a glass rod present.

In a given series of experiments at a fixed temperature, ignition tests with hydrocarbon fuels were always preceded and followed by ignition tests with ammonia to check that the surface was unchanged, since it was found that the ammonia-perchloric acid system was sensitive to small amounts of catalyst on the surface.

## 2.2 Materials

The perchloric acid was of analytical reagent grade. This contained 72% acid by weight (i.e.  $\text{HClO}_4$ ,  $2.17\text{H}_2\text{O}$ ) and is the constant boiling point mixture (b.p.  $203^\circ\text{C}$  at 1 atm).

The gaseous fuels were methane, ethylene (British Oxygen Company Limited), isobutene (Matheson Company Inc.) and ammonia (I.C.I. Limited). The solid fuels were carbon (active charcoal - Sutcliffe, Speakman & Company Limited, decolourizing charcoal - May and Baker Limited, and sugar charcoal - Hopkins and Williams Limited), nylon, terylene, polymethylmethacrylate (I.C.I. Limited), polystyrene, polyurethane rubber (both polyether and polyester types) and polyisobutene (as used in British plastic propellents). The polyisobutene was a viscous fluid and the polyurethanes were soft rubbers.

Substances used to test for catalytic activity were cupric chromate, ferric oxide, silica, alumina and titanium dioxide (Hopkins and Williams Limited).

All materials were used as received.

## 3 RESULTS

### 3.1 Solid fuels

The results of the experiments with perchloric acid vapour and oxygen on polyisobutene, polyurethane, polystyrene and polymethylmethacrylate are shown in Table 1. In addition, a few experiments were made using pyrolyzed perchloric acid vapour (27.4% by volume oxygen, 7.9% chlorine, 42% water and 22.8% argon) at 400 to  $440^\circ\text{C}$  but in no case was ignition achieved. It is seen from Table 1 that, whereas no ignitions were achieved with oxygen at temperatures in the range 200 to  $300^\circ\text{C}$ , all the fuels ignited with perchloric acid vapour in this range. With all fuels except polystyrene the ignition delays became small as the temperature approached  $300^\circ\text{C}$ . When the fuel samples were initially at ambient temperature ignitions were achieved in two cases, though with somewhat increased ignition delay times.

With oxygen ignitions were achieved only at temperatures well above  $300^\circ\text{C}$  and in some cases temperatures above  $400^\circ\text{C}$  were required. The results therefore show quite clearly that 72% perchloric acid vapour is a much stronger oxidizing agent than oxygen gas and readily ignites most propellant fuels at the temperature prevailing at the propellant surface.



Experiments were also made using perchloric acid with less volatile fuels. Carbon, nylon and terylene were used as examples of fuels with low vapour pressures at 200-250°C. Since some of these experiments were made with apparatus B, polyurethane rubber and polymethylmethacrylate were also used to permit a comparison with the results obtained from apparatus A. The carbon came from four sources - two samples were activated charcoal (one from an unidentified source), one was decolourizing charcoal and the fourth was sugar charcoal. These were heated to 500°C for 2½ hours before use to ensure that any readily volatile materials were removed.

The results obtained with perchloric acid vapour are shown in Table 2. The finely divided charcoal ignited rapidly but lumps of sugar charcoal would not ignite at 200°C. The other fuels all ignited readily except for terylene which presented some difficulty.

### 3.2 Gaseous fuels

Ammonia, methane, ethylene and isobutene were used as gaseous fuels. Ammonia was chosen because it is produced when ammonium perchlorate is vaporized<sup>4,5</sup>. The others were chosen because it has been shown<sup>12</sup> that polyisobutene, a fuel in British plastic propellants, is pyrolyzed to yield isobutene at about 350°C, and also methane and ethylene at about 475°C. Polyisobutene was not used as a fuel in these experiments because, on exposure to perchloric acid vapour, it chars badly and becomes mobile.

Ignition delays with perchloric acid vapour are shown in Table 3 and in the presence of a catalyst in Table 4. No ignitions were observed in the absence of a surface (experimental arrangement C). Introduction of a glass rod (D) caused ignition to occur only with ammonia and isobutene.

At 220°C with a heated ceramic plate (B), ammonia ignited after a short delay, isobutene ignited occasionally with a long delay, and methane and ethylene would not ignite. However, at 290°C the situation was somewhat more distinct; ammonia ignited after a short delay (<2 sec), isobutene ignited after a longer delay (<30 sec), ethylene generally would not ignite (>300 sec), and methane did not ignite at all.

The same order of ignitability was observed in the presence of a catalyst (copper chromate). Ammonia at 200-300°C would ignite rapidly with no noticeable delay, ignition occurring as the fuel and oxidizer tubes were swung together.

At 290°C isobutene ignited with a short delay (~0.2 sec), ethylene ignited after a long delay (~30 sec), and methane would not ignite. Ferric oxide was as effective a catalyst for the ammonia-perchloric acid ignition as cupric chromate, but titanium dioxide, silica and alumina did not effect detectable reductions in the ignition delays.

Whenever ignition was achieved, combustion was always sustained.

An interesting observation was that cupric chromate, placed on a cold spatula or glass rod and introduced into a jet of ammonia at 290°C would glow and give sparks after a delay of about 7 seconds. An even shorter delay (<1 sec), was observed if the cupric chromate was preheated. However, since the ignition delay of ammonia and perchloric acid in the presence of cupric chromate was much less than that required to initiate the glow, this phenomenon may be neglected in evaluating the results. Only when the cupric chromate was preheated (~290°C) did a similar glow appear with isobutene. No glow was observed with methane and ethylene.

#### 4 DISCUSSION

The theory of the ignition of solid propellents has recently been thoroughly reviewed<sup>13</sup>. There are three contending theories - the solid, heterogeneous, and gas-phase ignition theories. The solid phase theory was developed primarily for double-base propellents and is much less plausible for composite ammonium perchlorate propellents. Subsequently, Summerfield et al<sup>1</sup> developed the gas-phase model in which a hot oxidizing environmental gas and fuel vapours from the propellant mixed and reacted to produce ignition. On the other hand, Anderson et al<sup>2</sup> developed the heterogeneous theory as a result of experiments on the hypergolic ignition of propellents with such oxidizers as fluorine and chlorine trifluoride. It postulates that the oxidizer is decomposed by external heating, and the resulting gaseous products then attack the solid fuel surface.

The present work with fuels used in composite propellents has shown that ignition can occur rapidly at the decomposition temperature of ammonium perchlorate and that it is not necessary for the perchloric acid-fuel mixture to become further heated by diffusing from the propellant surface into the hotter igniter gases. However, this same work does not permit one to deduce whether the important exothermic reactions, which lead to ignition, occur between perchloric acid vapour and either the solid fuel or the vaporized fuel.

Two approaches to the solution of this question have been made. First, ignition studies have been carried out with less volatile fuels - carbon, nylon and terylene. Since these can be ignited and, in particular, because finely divided carbon reacts rapidly, this strongly suggests that heterogeneous reactions lead to ignition. This is to be compared with the heterogeneous mechanism recently proposed<sup>14,15</sup> for the ignition of pulverized coal particles in air at a temperature of about 1000°C. It has recently been determined<sup>16</sup> that the vapour pressure of the polyisobutene was about 7 mm Hg at 250°C. This low value gives additional support for a heterogeneous mechanism, although it is known that the resulting acid-rich mixture would be flammable<sup>11</sup>.

The second approach has been to study the ignition characteristics of the gaseous species expected to be present above an ammonium perchlorate - polyisobutene propellant (i.e. plastic propellant) and to determine the effect of surfaces and catalysts upon these ignition characteristics. The gaseous species used were those known to be formed in the pyrolysis of polyisobutene<sup>12</sup> (isobutene, methane and ethylene), along with ammonia.

It has been shown that the ignition of gaseous fuels with perchloric acid vapour is much slower than that of the solid fuel which would form these gaseous fuels by pyrolysis. Consequently, this again strongly suggests that heterogeneous reactions lead to ignition in a propellant containing ammonium perchlorate.

The ignition of a composite ammonium perchlorate propellant may now be considered in more detail. After the igniter has fired, the temperature of the ammonium perchlorate and the fuel at the surface starts to rise. The ammonium perchlorate will vaporize and decompose to ammonia and perchloric acid, and the fuel will vaporize and pyrolyze to give a mixture of simple hydrocarbons and fuel monomer. There are several possible reactions by which such a system may proceed to ignition and these are outlined:

(i) ignition by gaseous reactions

e.g. perchloric acid - ammonia

perchloric acid - fuel monomer

perchloric acid - simple hydrocarbons,

(ii) ignition by gaseous reactions in the presence of a catalytic surface

e.g. perchloric acid - ammonia - catalyst

perchloric acid - monomer - catalyst,

and (iii) ignition by heterogeneous reactions

s.g. perchloric acid - solid fuel

perchloric acid - ammonium perchlorate.

A fourth possible route to ignition is by exothermal reactions occurring in the solid<sup>13</sup>, but this is not considered relevant to composite propellants.

It is to be emphasized that groups (ii) and (iii) include the heterogeneous decomposition of perchloric acid vapour to chlorine oxides, which may subsequently react either homogeneously with gaseous fuels or heterogeneously with solid fuel.

It has been shown that ignition by reactions in group (i) are much slower at low temperatures than in groups (ii) and (iii). In group (ii) it has been shown that the perchloric acid - ammonia - catalyst system ignites much faster than the perchloric acid - gaseous hydrocarbon - catalyst system. In group (iii) the reaction perchloric acid - solid fuel is much faster under the experimental conditions used than is perchloric acid - ammonium perchlorate. Ignition has not been observed in the present study by passing perchloric acid vapour over solid ammonium perchlorate, although Osada and Kakinouchi<sup>17</sup> have recently reported differential thermal analysis data in which addition of small quantities (~0.1 cc) of perchloric acid (60%) to ammonium perchlorate resulted in explosion at 250°C. They have also shown by differential thermal analysis that a polybutadiene rubber - perchloric acid mixture will ignite at 190°C. This is in agreement with our results with perchloric acid vapour.

It was found experimentally that perchloric acid - ammonia - catalyst mixtures ignited faster than perchloric acid - solid fuel mixtures. Since, in the practical case of an ammonium perchlorate propellant, the ammonia and perchloric acid will be vaporized together it seems probable that in the catalyzed propellant ignition will occur as a result of heterogeneous reactions between the ammonia and perchloric acid vapour on the surface of the catalyst. The alternative route would involve diffusion of the perchloric acid vapour back to the fuel surface before heterogeneous reaction could occur and this appears less probable. In an uncatalyzed propellant it is likely that both the perchloric acid - ammonia reaction on the propellant surface and the perchloric acid - solid fuel reaction lead to ignition. In this case the ambient pressure probably determines which reaction is dominant. High pressure would favour the perchloric acid - ammonia reaction since it would inhibit diffusion of the perchloric acid back to the fuel surface. This conclusion is

in agreement with the combustion mechanism<sup>7</sup> proposed for a composite propellant at high pressure, which requires a premixed perchloric acid - ammonia flame close to the surface of the ammonium perchlorate crystal.

The catalysis of the perchloric acid - ammonia reaction by either cupric chromate or ferric oxide is in accord with the observations that these substances are effective catalysts in the ignition of propellents<sup>18,19,20</sup>. The inert natures of titanium dioxide, silica and alumina are also in agreement with previous work on the ignition of ammonium perchlorate<sup>21</sup>.

The present findings give strong support to the conclusions made by Wise et al<sup>18</sup> as a result of experiments on the ignition of ammonium perchlorate - copper chromite mixtures in an arc image furnace. They concluded that when ignition occurred by reactions involving gaseous species, the critical species was perchloric acid, and that the copper chromite promoted ignition by catalysing the decomposition of perchloric acid, which could then react with gaseous fuel.

Wise has also shown<sup>18</sup> that at high heat fluxes, similar to those occurring in practice, higher surface temperatures must be considered. It is assumed that the present findings may be extrapolated to this higher temperature range. However, Levy<sup>22</sup> has shown that in a quartz vessel the homogeneous decomposition of perchloric acid vapour predominates over the heterogeneous decomposition at temperatures in excess of 310°C. Thus it might be expected that homogeneous gas phase reactions will be increasingly important at these higher temperatures. Nevertheless, in the case of ignition of a solid propellant the surfaces available for heterogeneous reactions will be more active than a quartz surface. Therefore, the transition from heterogeneous to homogeneous decomposition will be expected at a much higher temperature than that found by Levy.

To summarize, although the homogeneous gas phase theory of solid propellant ignition proposed by Summerfield et al<sup>1</sup> is valid under their experimental conditions (oxygen gas under pressure in a shock tube) the present work suggests that it is invalid for composite solid propellant ignition in a rocket motor. On the other hand, for this latter case, the heterogeneous theory suggested by Anderson et al<sup>2</sup> is probably valid, but it is unlikely to be so for ignitions in a shock tube containing gaseous oxygen.

## 5 CONCLUSIONS

Non-volatile fuels such as carbon readily ignite with perchloric acid vapour at 200 to 300°C. At these temperatures gaseous fuels ignite only in

Table 1

Ignition delays of polyisobutene (PIB), polyurethane (PU), polystyrene (PS), and polymethylmethacrylate (PMI) with oxygen and perchloric acid vapour

Fuel	Oxidizer	Ignition delay	Temperature, °C		Remarks <sup>a</sup>
			Oxidizer	Fuel	
PIB	Oxygen	<1 sec	441	430	average of 3
		60 sec	357	347	
	O <sub>2</sub> /Ar (15:10)	<1 sec	444	451	average of 2
		<1 sec	407	426	average of 3
		29 sec	407	407	average of 2
		3 min 19 sec	351	334	average of 2
	Perchloric acid (72%)	<1 sec	288	272	average of 2
		23.5 sec	258	208	
		19 sec	179	200	
		no ign.	212	20	
PU	Oxygen	23 sec	429	417	average of 2
		>3 min no ign.	353	345	
	O <sub>2</sub> /Ar (15:10)	60 sec	448	455	average of 4
		94 sec	424	441	average of 2
		>5 min no ign.	343	317	
	Perchloric acid (72%)	<1 sec	295	248	average of 2
		<1 sec	251	211	
		4 sec	179	213	
		<1 sec	295	18	average of 4
		9 sec	295	18	
		4.5 sec	214	20	
PS	Oxygen	50 sec	442	457	
		>4 min no ign.	357	343	
	O <sub>2</sub> /Ar (15:10)	>5 min no ign.	455	447	average of 3
	Perchloric acid (72%)	38 sec	300	270	average of 2 120 sec preheat
		83 sec	300	278	
		24.5 sec	249	220	
		158 sec	255	224	
		>5 min no ign.	258	215	
		>3 min no ign.	296	18	
		>5 min no ign.	208	20	
PMI	Oxygen	>3 min no ign.	442	445	average of 4 red glow
		>3 min no ign.	360	345	
	Perchloric acid (72%)	2.2 sec	303	270	average of 2
		7 sec	245	217	average of 2
		10 sec	304	18	average of 2
		20 sec	237	19	average of 2

<sup>a</sup>Apparatus A was used throughout  
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Table 2

Ignition delays of solid fuels with perchloric acid vapour

Fuel	Apparatus	Ignition delay, sec	Temperature, °C		Remarks
			Oxidizer	Fuel	
Active charcoal (I)	A	<1	254	229	average of 2
		<1	231	230	average of 2
Active charcoal (II)	A	<1	241	221	
		<1	220	202	
Decolourizing carbon	A	<1	242	232	
		<1	225	204	
Sugar charcoal	B	<1	203	188	
		<1	203	193	fine powder
Nylon	A	1.8	261	251	
		22.2	219	205	
Terylene	A	15.8	261	239	} difficult to ignite
		>180 no ign.	219	209	
Polymethylmethacrylate	B	0.5	287	291	average of 2
		3.2	262	241	average of 3
		6.6	219	204	average of 2
Polyurethane (polyether)	B	0.5	203	184	average of 3
Polyurethane (polyester)	B	0.5	203	186	average of 2

Table 3

Ignition delays of gaseous fuels with perchloric acid vapour

Fuel	Apparatus	Ignition delay, sec	Temperature, °C			Remarks
			Acid	Fuel	Surface	
NH <sub>3</sub>	C	No ign. >300	210	200	-	
C <sub>2</sub> H <sub>4</sub>	C	No ign. >300	210	200	-	
NH <sub>3</sub>	D	18.2	210	200	-	average of 7
C <sub>2</sub> H <sub>4</sub>	D	No ign. >120	210	200	-	
NH <sub>3</sub>	C	No ign. >180	270	265	-	
Isobutene	C	No ign. >180	270	265	-	
C <sub>2</sub> H <sub>4</sub>	C	No ign. >180	270	265	-	
NH <sub>3</sub>	D	20.7 <sup>a</sup>	270	265	-	average of 2
Isobutene	D	61.3	270	265	-	average of 2
C <sub>2</sub> H <sub>4</sub>	D	No ign. >180	270	265	-	
NH <sub>3</sub>	B	4.2	205	190	225	average of 29
CH <sub>4</sub>	B	No ign. >180	205	190	225	
C <sub>2</sub> H <sub>4</sub>	B	No ign. >300	205	190	225	average of 2
Isobutene	B	42.5	205	190	225	average of 4 <sup>b</sup>
NH <sub>3</sub>	B	3.5	210	200	220	average of 9
NH <sub>3</sub>	B	1.1	275	260	290	average of 10
CH <sub>4</sub>	B	No ign. >300	270	260	295	average of 2
C <sub>2</sub> H <sub>4</sub>	B	No ign. >300	275	260	290	average of 2 <sup>c</sup>
Isobutene	B	32.2	275	260	290	average of 13
NH <sub>3</sub>	B	0.6	275	260	290	average of 12

<sup>a</sup>The position of the glass rod varied slightly in each test, hence this somewhat high value.

<sup>b</sup>In two cases ignition did not occur (>240 sec).

<sup>c</sup>Ignition occasionally occurred but was not reproducible.

Gas flow for each test was:

fuel	10	cc sec <sup>-1</sup>
perchloric acid	5	cc sec <sup>-1</sup>
argon	10	cc sec <sup>-1</sup>
water	10.8	cc sec <sup>-1</sup>



Table 4

Ignition delays of gaseous fuels with perchloric acid  
vapour in presence of catalyst

Fuel	Apparatus	Catalyst	Ignition delay, sec	Temperature, °C			Remarks
				Acid	Fuel	Surface	
NH <sub>3</sub>	D	CC <sup>a</sup>	No delay	210	200	-	average of 2
C <sub>2</sub> H <sub>4</sub>	D	CC	No ign. >180	210	200	-	average of 2
NH <sub>3</sub>	B	CC	No delay	220	200	220	average of 4
Isobutene	B	CC	3	220	200	220	average of 3 <sup>b</sup>
C <sub>2</sub> H <sub>4</sub>	B	CC	No ign. >300	220	200	220	average of 2
NH <sub>3</sub>	B	CC	No delay	280	265	290	average of 4
Isobutene	B	CC	~0.2	280	265	290	average of 5
C <sub>2</sub> H <sub>4</sub>	B	CC	31.2	270	260	295	average of 9
CH <sub>4</sub>	B	CC	No ign. >300	270	260	295	average of 2
NH <sub>3</sub>	B	None	3.3	225	205	225	average of 6
NH <sub>3</sub>	B	CC	No delay	225	205	225	average of 3
NH <sub>3</sub>	B	TiO <sub>2</sub>	4.1	225	205	225	average of 4
NH <sub>3</sub>	B	Fe <sub>2</sub> O <sub>3</sub>	No delay	225	205	225	average of 3
NH <sub>3</sub>	B	Al <sub>2</sub> O <sub>3</sub>	4.6	225	205	225	average of 5
NH <sub>3</sub>	B	SiO <sub>2</sub>	3.0	225	205	225	average of 8
NH <sub>3</sub>	D	CC	No delay	210	200	-	average of 2
NH <sub>3</sub>	D	CC	7.0	- <sup>c</sup>	265	-	average of 3
NH <sub>3</sub>	B	CC	No delay	- <sup>c</sup>	275	285	average of 2

<sup>a</sup>Cupric chromate.

<sup>b</sup>An aging effect of the catalyst was observed (possibly due to acid attack); aged catalyst caused ignition at 137 sec in one case and no ignition (>180 sec) in another. However, this catalyst was still effective with ammonia.

<sup>c</sup>No perchloric acid present.

Gas flows were as in Table 3.

REFERENCES

- | <u>No.</u> | <u>Author</u>                                       | <u>Title, etc.</u>  |
|------------|---|---|
| 1          | R. F. McAlevy, III<br>P. L. Cowan<br>M. Summerfield | The mechanism of ignition of composite solid propellants by hot gases.<br>Solid Propellant Rocket Research, Vol.1 of A.R.S. Series on Progress in Astronautics and Rocketry, pp.623-652, New York, Academic Press, 1960           |
| 2          | R. Anderson<br>R. S. Brown<br>L. J. Shannon         | Heterogeneous reactions in ignition and combustion of solid propellants.<br>A.I.A.A. Journal, <u>2</u> (1964), No.1, 179-180  |
| 3          | R. F. McAlevy, III<br>S. Y. Lee<br>R. S. Magee      | The solid propellant ignition mechanism: a simple diagnostic experiment.<br>Astronautica Acta, <u>11</u> (1965), No.2, 144-145  |
| 4          | S. H. Inami<br>W. A. Rosser<br>H. Wise              | Dissociation pressure of ammonium perchlorate.<br>J. Phys. Chem., <u>67</u> (1963), No.3, 1077-1079   |
| 5          | J. L. Mack<br>A. S. Tompa<br>G. B. Wilmot           | Matrix isolation and infra-red determination of the vapour species of $\text{NH}_4\text{ClO}_4$ .<br>Symp. on Molecular Structure and Spectroscopy, Ohio State Univ., 1962; Abstract in Spectrochim. Acta, <u>18</u> (1962), 1375 |
| 6          | M. E. Baicar<br>W. G. Gough<br>E. F. Hare           | An apparatus for the differential thermal analysis of explosives.<br>U.S. Naval Propellant Plant Technical Report 114. NAVJEPs Report 7107, December 1961   |
| 7          | J. Powling  | The combustion of ammonium perchlorate - based composite propellents: A discussion of some recent experimental results.<br>E.R.D.E. Report No. 15/R/65, July 1965   |
| 8          | G. A. McD. Cummings<br>A. R. Hall                   | Perchloric acid flames: I, Premixed flames with methane and other fuels.<br>Tenth (International) Symposium on Combustion, pp.1365-1372, Pittsburgh, The Combustion Institute, 1965   |

REFERENCES (CONT'D)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
9	W. Dietz	Über die Ungefährlichkeit konstant siedender 72%-iger Überchlorsäure. Angew. Chem., <u>52</u> (1939), 616-618 R.P.E. Translation No.8, January 1964
10	G. S. Pearson	Discussion on Ref.8 (see p.1371)
11	G. A. McD. Cummings	Perchloric acid decomposition flame. Combustion and Flame, <u>8</u> (1964), No.3, 199-202
12	B. C. Howard	The pyrolysis of some composite propellant fuel binders. E.R.D.E. Report No. 13/R/65, April 1965
13	E. W. Price H. H. Bradley, Jr. G. L. Dehority H. M. Ibiricu	Theory of ignition of solid propellants. A.I.A.A. Preprint No.66-64, January 1966
14	J. B. Howard R. H. Essenhigh	The mechanism of ignition of pulverized coal. Combust. Flame, <u>9</u> (1965), 337-339
15	J. B. Howard R. H. Essenhigh	Combustion mechanism in pulverized coal flames. Combust. Flame, <u>10</u> (1966), 92-93
16	D. Sutton P. C. Wellings	Unpublished work, 1966
17	H. Osada N. Kakinouchi	Initiation of ignition of solid composite propellents. Kogyo Kayaku Kyokaishi, <u>26</u> (1965), 200-211 T.I.L. Translation 5669 (1966)
18	W. A. Rosser N. Fishman H. Wise	Ignition of simulated propellants based on ammonium perchlorate. Stanford Res. Inst., Menlo Park, California, Report No. PU-3573, July 1965 also Astia Document No. AD 619, 067
19	D. Sutton P. C. Wellings	The ignition of solid propellents by radiant energy. R.P.E. Tech. Report No. 66/4, April 1966

REFERENCES (CONT'D)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
20	R. Anderson R. S. Brown G. T. Thompson R. W. Ebeling	Theory of Hypergolic ignition of solid propellants. A.I.A.A. Preprint 63-514 (December 1963)
21	F. Solymosi	Initiation of ammonium perchlorate - ignition by chromic oxide-titanium dioxide catalysts. Combust. Flame, <u>9</u> (1965), 141-148
22	J. B. Levy	The thermal decomposition of perchloric acid vapour. J. Phys. Chem. <u>66</u> , 1092-7 (1962)

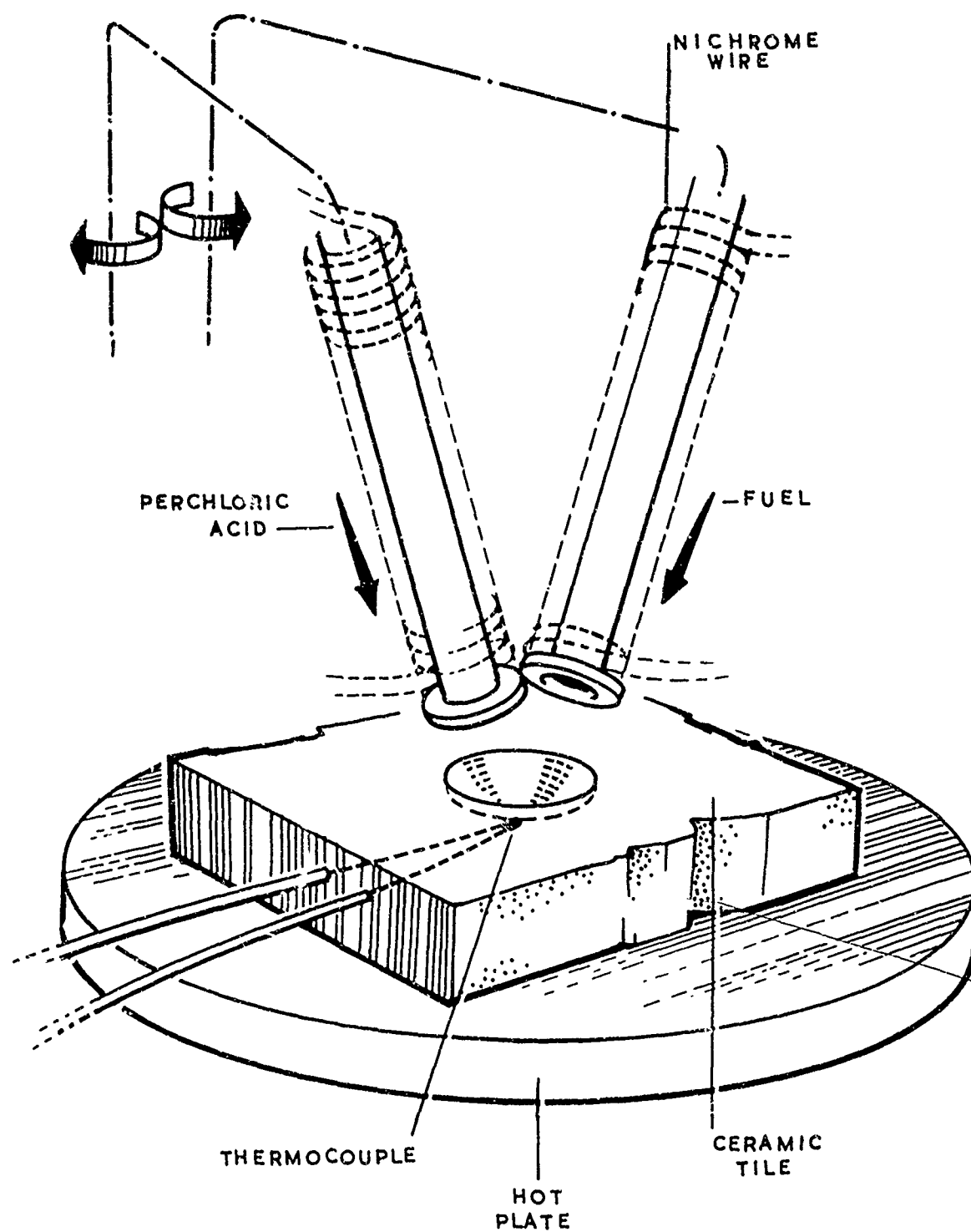


FIG. 1 APPARATUS FOR STUDY OF PERCHLORIC ACID IGNITION WITH GASEOUS FUELS